



Efficient catalytic systems for the carboxylation of diamines to cyclic ureas using ethylene urea as a promoter

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ABSTRACT

The carboxylation of diamines to cyclic ureas by CO₂ in the presence of an alkali metal carbonate or alkali metal bicarbonate exhibits a typical autocatalysis behavior, in which the rates of corresponding cyclic urea formations increase with time as in a S-shaped curves. The activity of the alkali metal carbonate was greatly enhanced when ethylene urea was co-present. Computational calculation results on the carboxylation of ethylenediamine in the co-presence of KHCO₃ and ethylene urea suggest that ethylene urea of keto form could tautomerize into enol form with the aid of KHCO₃ at least to a certain extent, thereby playing a role as a proton donor. With such transformation and the consequent favorable hydrogen bonding interaction with KHCO₃, the proton accepting and donating abilities of KHCO₃ can be enhanced and, as a result, the carboxylation is accelerated.

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1. Introduction

The synthesis of cyclic ureas using CO₂ has gained recent interest in view of the utilization of a greenhouse gas [1–3], as well as their wide variety of applications as intermediates of pharmaceuticals, cosmetics, pesticides, urethanes, and etc. [4,5]. In particular, dimethylol ethylene urea, prepared from the condensation of formaldehyde with ethylene urea (imidazolidine-2-one or 2-imidazolidone), is industrially used in large quantities for wrinkle-resistance finish in cotton fabrics [6,7]. Ethylene urea also finds uses as a scavenging agent to remove free formaldehyde in phenolic, melamine, glyoxal and urea formaldehyde resin systems for the coatings, constructions and textile industries. Cyclic ureas can be prepared from the oxidative carbonylation of 1,2-diamines and 1,3-diamines followed by cyclization [8,9]. However, the use of oxidative carbonylation method requires extreme care due to the explosion hazard associated with the co-use of CO and an oxidant, O₂ [10,11]. As an alternative approach, urealysis of diamines at elevated temperatures around 250 °C and/or high pressures above 12 atm has been investigated, but the process has some drawbacks

such as the handling of co-produced ammonia and the equipment corrosion [12,13].

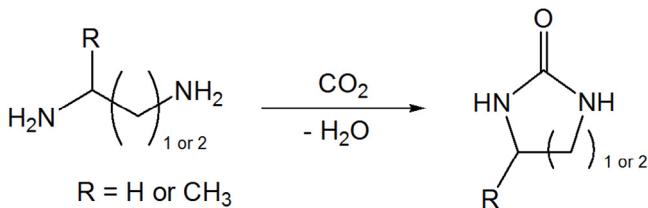
In view of this, the manufacture of cyclic ureas using nontoxic and noncorrosive CO₂ as a carbonyl source in the manufacture of cyclic ureas would be highly attractive (Scheme 1) [14,15]. Much effort has been devoted to the development of synthetic processes of cyclic ureas from the direct carboxylation reaction of diamines [2,16–20]. Accordingly, a number of catalysts have been developed, including tungsten-based polyoxometalates, superbase along with an electrophile, PEG-supported alkali metal hydroxide, triphenylstibine oxide, triphenylantimony oxide and CeO₂-based catalysts [2,17–20]. Of these, the catalytic systems based on CeO₂ are of particular interest regarding on the catalyst separation and recycling. Cyclic ureas have also been prepared non-catalytically from the carboxylation of diamines, but with low turnover frequency numbers [5]. Despite the significant advances made so far in the synthesis of cyclic ureas from the reactions of diamines with CO₂, much remains to be ameliorated, especially in view of cyclic urea productivity and/or catalyst activity.

We now report that the carboxylation of diamines to cyclic ureas can be greatly facilitated when a base catalyst such as an alkali metal carbonate or alkali metal bicarbonate is used along with ethylene urea. The role of ethylene urea in the carboxylation of diamines is also discussed in detail.

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Scheme 1. Synthesis of cyclic ureas from the carboxylation of diamines by CO_2 .

2. Experimental

2.1. General

Diamines including ethylenediamine (EDA), 1,2-propanediamine (1,2-PDA), 1,3-propanediamine (1,3-PDA) were purchased from Aldrich Chemical Co. and used as received. To remove water, alkali metal carbonates and alkali metal bicarbonates, obtained from Aldrich Chemical Co., were dried at suitable temperatures under vacuum before use. Carbon dioxide (purity > 99.9%) was used without further purification.

2.2. Carboxylation of diamines

All carboxylation experiments were conducted in 100 mL stainless steel bomb reactor. In a typical experiment, the reactor was charged with EDA (100 mmol), 1-methyl-2-pyrrolidinone (NMP, 20 mL), KHCO_3 (0.5 mmol), and dioxane (2.00 g) as an internal standard, and flushed with 1.0 MPa CO_2 three times. The reactor was then heated to 200 °C under pressure of 1.0 MPa CO_2 . The CO_2 pressure was increased to 5.0 MPa at 200 °C and maintained throughout the reaction for 2 h. After the period of the reaction, the reactor was immersed in an iced bath cooled at 0 °C and then depressurized. The organic product mixture was dissolved in methanol and analyzed by NMR spectroscopy (400 MHz, Bruker), a gas chromatograph (GC, Agilent 6890, FID, DB-5 capillary column), and a GC-Mass spectrometer (Agilent 6890-5973, HP-MS capillary column). The characterization of the solid product was made on a X-ray diffractometer (Rigaku, D/Max-III) and FT-IR spectrometer (Nicolet iS10).

2.3. Quantum mechanical calculations

All calculations on the KHCO_3 -catalyzed carboxylation of EDA by CO_2 were carried out in Gaussian 09 [21]. Geometries were optimized with the hybrid Becke3-Lee-Yang-Parr (B3LYP) exchange-correlation functional with the 6-31+G* basis sets for C, H, N, O and K. All kinds of possible interaction patterns were optimized using reasonable starting geometries to ensure global minimum. All the geometries optimized were also subjected to full frequency analyses at the same level of theory to verify the nature of the stationary points. Equilibrium geometries were characterized by the absence of imaginary frequencies. B3LYP enthalpy and entropy corrections were used for all thermodynamic corrections. The effect of bulk solvent was also taken into account in the single point calculations through the self-consistent reaction field theory (SCRF) based on the Polarizable Continuum Model (IEPCM-UFF) implemented in the Gaussian 09 program. Since NMP is not available in the program package, *N,N*-dimethylacetamide (DMA) was used instead in the calculation.

Table 1
Effect of reaction time on the carboxylation of EDA by CO_2 .^a

Time (h)	Yield (%)		
	Without catalyst	KHCO_3	K_2CO_3
0.5	6.4	25.1	29.0
1	9.6	27.7	34.6
1.5	15.6	32.3	40.3
2	21.1	38.8	48.2
2.5	21.4	53.2	68.4
3	21.5	69.8	82.7
3.5	21.8	81.5	88.3
4	22.3	87.5	91.7

^a Reaction condition: molar ratio of EDA/catalyst = 100, solvent = NMP, P_{CO_2} = 5 MPa, reaction temperature = 200 °C.

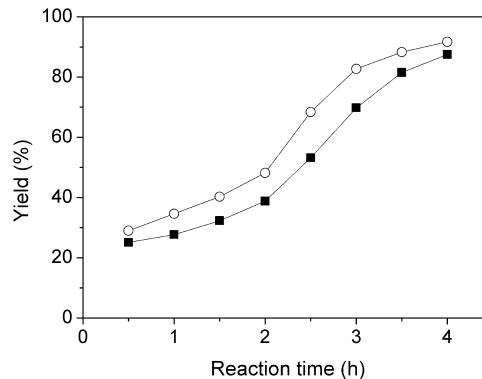


Fig. 1. Effect of reaction time on the carboxylation of EDA by CO_2 in the presence of (-■-) KHCO_3 and (-○-) K_2CO_3 . Reaction condition: EDA (100 mmol), molar ratio of EDA/catalyst = 100, solvent (NMP, 20 mL), P_{CO_2} = 5 MPa, reaction temperature = 200 °C.

3. Results and discussion

3.1. Synthesis of ethylene urea

The synthesis of cyclic ureas from the carboxylation of diamines by CO_2 was investigated in the presence of a base catalyst (Scheme 1). Interestingly, we have observed that the rate of ethylene urea formation increases sharply after a certain period of reaction time, yielding a S-shaped curve, when the carboxylation of EDA was conducted using KHCO_3 as the catalyst (see Table 1 and Fig. 1). This is a typical phenomenon observed in various autocatalytic reactions [22]. It is most likely that ethylene urea formed during the carboxylation functions as a catalyst or a promoter in the carboxylation reaction of EDA. If the carboxylation is accelerated by ethylene urea produced during the carboxylation, the addition of ethylene urea in the beginning of the reaction should promote the carboxylation of EDA.

As listed in Table 2, the yields of ethylene urea were found at around 40% except Cs_2CO_3 and CsHCO_3 for the catalytic carboxylations of EDA conducted at 200 °C for 2 h. To our expectation, the yield of ethylene urea in the presence of KHCO_3 increases dramatically by 33.5% from 38.8 to 72.3% by the addition of small amounts of ethylene urea to a reaction mixture. Similar behaviors were also observed when the carboxylation was conducted in the presence of other alkali metal carbonate or bicarbonate catalyst including K_2CO_3 , Cs_2CO_3 , or CsHCO_3 , indicating that ethylene urea functioned as a promoter for the carboxylation. In particular, the yield of EDA was almost quantitative when CsHCO_3 or Cs_2CO_3 was used as the catalyst along with ethylene urea. As listed in Table 2, the promoting effect of ethylene urea was also evident for the carboxylations of EDA with less active catalysts including sodium acetate (NaOAc), 1-butyl-3-methylimidazolium chloride ($[\text{BMIm}] \text{Cl}$) and

Table 2Catalytic activities of various catalysts for the carboxylation of EDA by CO_2 .^a

Entry	Catalyst	Ethylene urea yield (%)	
		Without added ethylene urea	With added ethylene urea ^b
1	none	21.1	23.4
2	KHCO_3	38.8	72.3
3	K_2CO_3	48.2	76.5
4	K_3PO_4	51.3	77.8
5	Cs_2CO_3	73.4	98.2
6	CsHCO_3	71.6	96.5
7	NaOAc	34.3	64.8
8	$[\text{BMIm}] \text{Cl}$	31.8	47.3
9	Bu_4PBr	35.8	53.2

^a Reaction condition: EDA (100 mmol), molar ratio of EDA/catalyst = 100, solvent (NMP, 20 mL), P_{CO_2} = 5 MPa, reaction temperature = 200 °C, reaction time = 2 h.^b amount of added ethylene urea = 1 g.

tetra-*n*-butylammonium bromide (Bu_4PBr). As a whole, the yield of ethylene urea increased by 15 – 30% when small amounts of ethylene urea was co-present with the catalyst.

One may suspect that the presence of ethylene urea would enhance the nucleophilicity or basicity of EDA via hydrogen bonding interaction between the carbonyl oxygen of ethylene urea and an amino hydrogen atom of EDA, thereby facilitating the reaction of the EDA with CO_2 . In general, the carboxylation of primary and secondary amines by CO_2 is known to proceed rapidly at room temperatures with almost no activation barrier, forming carbamate or carbonate species depending on the solvent employed. Therefore, in the reactions of amines with CO_2 , there is no need to enhance the basicity or nucleophilicity of EDA. It has been reported that the carboxylation of monoamines by CO_2 to substituted ureas proceeds via a series of protonation-deprotonation processes [23,24]. If this is the case for the carboxylation of diamines, the role of ethylene urea should be the one to facilitate the protonation and deprotonation steps in the catalytic cycle. Since added ethylene urea alone is not capable of promoting the carboxylations of EDA in the absence of a catalyst (Table 2, Entry 1), it seems reasonable to assume that the role of ethylene urea is to assist the catalyst, possibly in donating and accepting proton to and from the carboxylated intermediate species in a more facile manner, thereby facilitating the carboxylation.

3.2. Spectroscopic consideration

To have a clue on the promoting role of ethylene urea in the KHCO_3 -catalyzed carboxylation of diamines, we have synthesized deuterated ethylene urea by reacting EDA with deuterated urea (urea-*d*₄) [25], and used as a promoter in the carboxylation of 1,2-PDA to see if there is any deuterium incorporation in the product, 4-methylethylene urea. As shown in Fig. 2, the mass spectrum of the product, 4-methylethylene urea clearly reveals that 4-methylethylene urea is partially deuterated, indicating that H-D exchange takes place between deuterated ethylene urea and the product, 4-methylethylene urea. However, in the carboxylation of 1,2-PDA conducted with added deuterated ethylene urea in the absence of KHCO_3 , the deuterium incorporation in 4-methylethylene urea is almost negligible, implying that ethylene urea is able to function as a promoter only in the presence of the catalyst, and the H-D exchange is largely mediated by KHCO_3 .

Interaction of KHCO_3 with ethylene urea was also investigated by FT-IR spectroscopy. Fig. 3(a) is the FT-IR spectrum of KHCO_3 with a carbonyl absorption band at 1620 cm^{-1} , and Fig. 3(b) is the FT-IR spectrum of ethylene urea, which shows an intense carbonyl absorption band at 1645 cm^{-1} as well as a strong absorption peak at 3289 cm^{-1} assignable to N–H stretching frequency. When KHCO_3 and ethylene urea were mixed together, both of the carbonyl absorption peaks of KHCO_3 and ethylene urea became merged

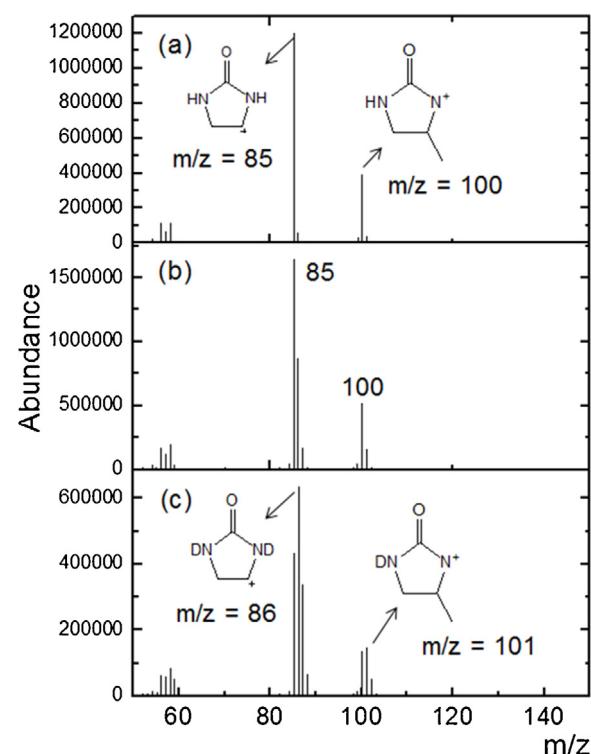


Fig. 2. GC-mass spectra of the carboxylation product of 1,2-PDA by CO_2 in the presence of (a) KHCO_3 , (b) deuterated ethylene urea, and (c) KHCO_3 and deuterated ethylene urea.

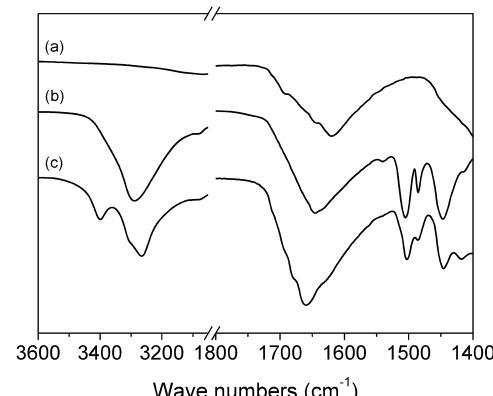


Fig. 3. FT-IR spectra of (a) KHCO_3 , (b) ethylene urea, and (c) ethylene urea and KHCO_3 .

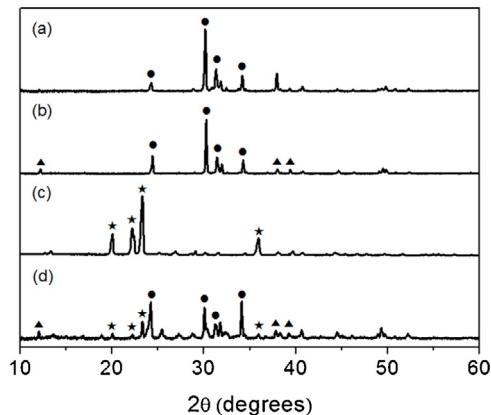


Fig. 4. XRD patterns of (a) KHCO_3 , (b) water-containing KHCO_3 , (c) ethylene urea, and (d) recovered catalyst ((●) KHCO_3 , (▲) KOH and (★) ethylene urea).

into a broad peak at higher frequency centered at 1660 cm^{-1} (Fig. 3(c)). One interesting feature observed for the interaction of KHCO_3 with ethylene urea is that the peak associated with the N–H stretching frequency is split into two peaks: one at considerably higher frequency of 3399 cm^{-1} and the other at lower frequency of 3265 cm^{-1} . Such a large N–H peak shift by 110 cm^{-1} from 3289 to 3399 cm^{-1} may suggest that N–H proton of ethylene urea is highly labile in the presence of a base catalyst, and thus the keto to enol transformation is also possible.

To see any change in the catalyst morphology, carboxylation of EDA was conducted with KHCO_3 at 200°C for 4 h and at the EDA/ KHCO_3 molar ratio of 10. After the period of the carboxylation, the slurry mixture was filtered and the recovered solid catalyst was characterized by XRD. To avoid the complexity incurred by the presence of the product and ethylene urea, the recovered catalyst was washed with CH_3OH and CH_2Cl_2 three times each. As shown in Fig. 4, XRD pattern of the recovered catalyst is apparently different from that of the fresh catalyst, KHCO_3 . However, careful analysis reveals that such difference is originated from the presence of water produced during the carboxylation reaction. In fact, the recovered catalyst shows the same XRD pattern as a mixture of KHCO_3 and water in a 1:1 molar ratio, suggesting that KHCO_3 is recyclable and remains unchanged.

3.3. Computational calculations

The role of ethylene urea in the KHCO_3 -catalyzed carboxylation of EDA was theoretically investigated. As ethylene urea is found to promote the base-catalyzed carboxylation of EDA, it is assumed that ethylene urea plays a role in assisting the catalytic function of the base, most possibly as a proton donor. However, it is unlikely that ethylene urea plays a role as a proton donor in its keto form. One way for ethylene urea to function as a proton donor is probably the tautomerization into enol form with the aid of KHCO_3 . It has been reported that several urea compounds including ethylene urea and thiourea undergo keto to enol tautomerization although the equilibrium shift toward the imidol (enol) form is not very favorable [26,27]. With this in mind, we have conducted theoretical investigation on the possible tautomerization of ethylene urea with or without the presence of KHCO_3 .

5 shows the optimized structures and energies of the transition states and intermediate species for the interconversion of ethylene urea from keto to enol form with or without the presence of KHCO_3 . In the absence of KHCO_3 , the activation energy (ΔG^\ddagger_{TS1}) and the Gibbs free energy of formation (ΔG_1) for the transformation of ethylene urea from keto to enol form were calculated to

be 54.3 and $18.7\text{ kcal mol}^{-1}$, respectively, demonstrating that such interconversion is not a feasible process for ethylene urea. On the contrary, in the presence of KHCO_3 , the energies (ΔG^\ddagger_{TS2} and ΔG_2) were greatly reduced to 20.9 and 6.1 kcal mol^{-1} , respectively, suggesting that keto to enol tautomerization could occur without much difficulty under the experimental condition. A strong interaction was observed between ethylene urea and KHCO_3 with Gibbs free energy of $-10.8\text{ kcal mol}^{-1}$. Such a strong interaction is believed to be responsible for the reduction of the activation energy and the stabilization of enol form. For comparison, the effect of bulk solvent was also considered. The energies calculated considering the solvent effect were provided in Figs. 5 and 6 along with those without solvent effect. The calculated energies are significantly lowered when solvent effect is considered. However, the effect of solvent seems to be overestimated because KHCO_3 is practically insoluble in DMA.

In Fig. 6, a reaction mechanism based on calculation was proposed for the carboxylation of EDA by CO_2 in the presence of KHCO_3 . A stable network structure with a Gibbs free energy of $-11.3\text{ kcal mol}^{-1}$ is observed for the interactions of the enol form of ethylene urea with KHCO_3 , CO_2 , and EDA.

The carboxylation of EDA leading to the formation of ethylene urea is likely to proceed in three steps. The first step is the interaction of EDA with CO_2 to form a carbamate intermediate species (**A1**), in which a stable hydrogen bonding network among KHCO_3 , enol form of ethylene urea, and zwitterionic carbamate species of EDA is observed. The reaction of EDA with CO_2 in NMP proceeds very rapidly at room temperature, producing zwitterionic carbamate species ($\text{H}_3\text{N}^+\text{CH}_2\text{CH}_2\text{NHCO}_2^-$) even in the absence of a catalyst [28]. However, in the presence of KHCO_3 , the zwitterionic carbamate species can be more stabilized through the hydrogen bonding network. The activation energy (ΔG^\ddagger_{TS1}) and the Gibbs free energy of formation (ΔG_1) for the formation of **A1** were calculated as 4.4 and $-11.4\text{ kcal mol}^{-1}$, respectively, implying that the first carbonation step proceeds very rapidly. In the optimized structure of the transition state (TS_{A1}), it can be clearly seen that the enol form of ethylene urea functions as a proton donor as well as an acceptor to and from KHCO_3 . The second step could be the attack of the $-\text{NH}_3^+$ group of the zwitterionic species on the carbonyl carbon of **A1** to form an intermediate species, **A2** with two C–N and two O–H bonds through the transition state TS_{A2} . Such a nucleophilic attack of $-\text{NH}_3^+$ can be substantially due to the strong hydrogen bonding interaction with the oxygen atom of KHCO_3 , thereby facilitating the loss of hydrogen atom from NH_3^+ . The activation energy (ΔG^\ddagger_{TS2}) and the Gibbs free energies of formation (ΔG_2) of keto and enol forms in the second step were calculated to be 27.2 , 0.9 and $20.8\text{ kcal mol}^{-1}$, respectively. The third step is the formation of the final product, **A3** through the proton transfer followed by the loss of H_2O . The transition state energy (ΔG^\ddagger_{TS3}) and the Gibbs free energy of formation (ΔG_3) of **A3** were calculated as 26.3 and $-37.5\text{ kcal mol}^{-1}$, respectively. Although the activation energy for the third step is apparently high, but such high activation energy can be easily overcome at elevated reaction temperatures around 200°C . Based on the calculation results, it is most likely that the primary role of ethylene urea in the base-catalyzed carboxylation of diamines is the proton donation to the catalyst through the transformation into the enol form. It is worth to mention here that the proton donor should be less acidic than CO_2 . Otherwise, the catalyst will be transformed into an inactive or a much less active species through the reaction with the proton donor. The driving force for the carboxylation of EDA leading to ethylene urea seems to be the 5-membered ring formation. The exceptionally high water stability of ethylene urea would also contribute to the equilibrium shift toward the formation of ethylene urea.

3.4. Effect of molar ratio of EDA/KHCO₃

The effect of catalyst loading on the carboxylation of EDA was investigated in NMP in the EDA/KHCO₃ molar ratio range of 50–2000 at 200 °C and at 5.0 MPa of CO₂ for 2 h. As can be seen in Fig. 7, the yield of ethylene urea decreased rapidly with increasing molar ratio up to 500 and then slowly decreased thereafter.

3.5. Effect of solvent

The effect of solvent was also conducted at 200 °C and at 5.0 MPa of CO₂ for 2 h in the presence of added ethylene urea for the KHCO₃-catalyzed carboxylation reaction of EDA. As listed in Table 3, aprotic polar solvents including NMP, N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) showed similar conversions at around 75%, but the selectivity to ethylene urea was varied much with the solvent. The selectivity was almost 100% in NMP, whereas the selectivity was reduced to about 65% in DMF and DMSO, produc-

Table 3

Effect of solvent on the carboxylation of EDA by CO₂ with the presence of added ethylene urea.^a

Solvent	EDA conversion (%)	Ethylene urea yield (%)
NMP	72.5	72.3
DMF	74.5	48.6
DMSO	75.2	48.3
CH ₃ CN	27.8	26.2
CH ₃ OH	5.2	4.9
IPA	2.3	2.3
THF	2.1	2.1
toluene	1.4	1.4
CH ₂ Cl ₂	0.6	0.6

^a Reaction condition: EDA (100 mmol), molar ratio of EDA/KHCO₃ = 100, solvent (20 mL), P_{CO₂} = 5 MPa, reaction temperature = 200 °C, reaction time = 2 h, amount of added ethylene urea = 1 g.

ing considerable amounts of solvent-derived side products. The carboxylation of EDA was greatly suppressed in alcohol solvents

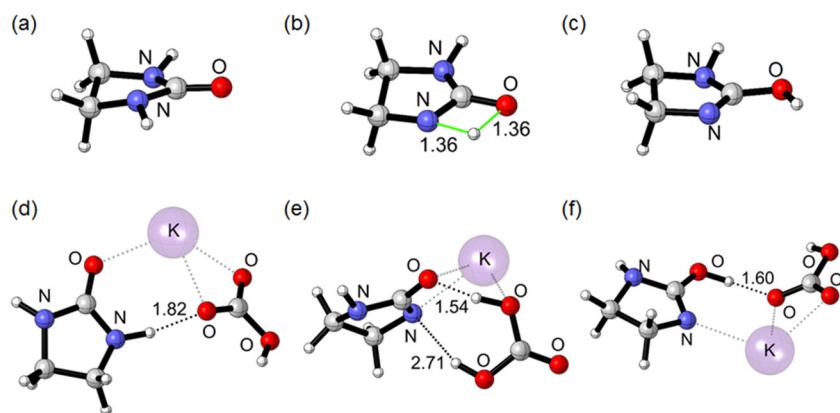


Fig. 5. Optimized structures for the interconversion of ethylene urea without KHCO₃: (a) keto form ($\Delta G = 0.0, -8.6$), (b) transition state ($\Delta G^{\ddagger, TS1} = +54.3, +48.2$), (c) enol form ($\Delta G_1 = +18.7, -6.0$), and those with KHCO₃: (d) keto complex ($\Delta G = -10.8, -32.7$), (e) transition state ($\Delta G^{\ddagger, TS2} = +20.9, -3.9$), (f) enol complex ($\Delta G_2 = +6.1, -14.8$). The two numbers in each parenthesis are energies calculated without and with solvent effect, respectively (energies are in kcal mol⁻¹).

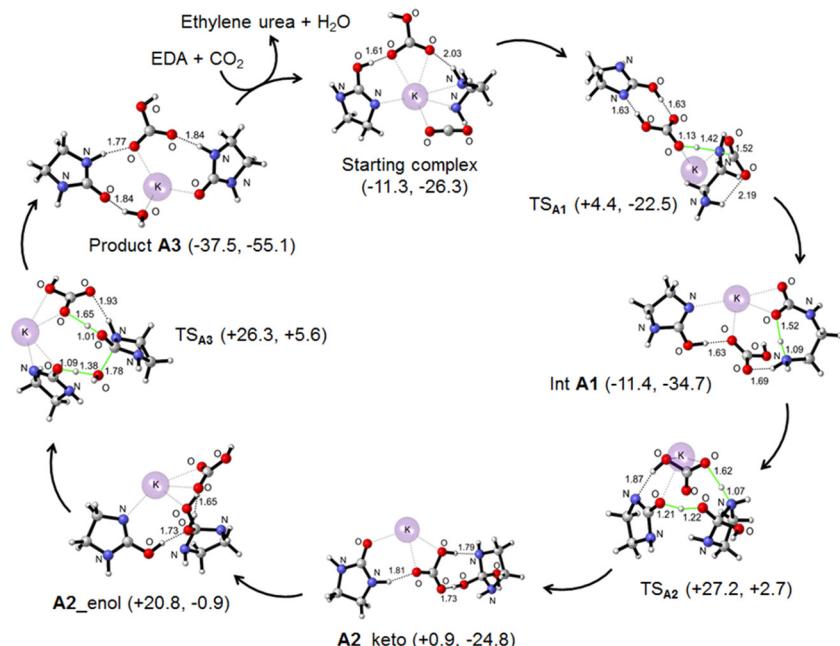


Fig. 6. Optimized structures of intermediates and transition states involved in the carboxylation of EDA by CO₂ in the presence of KHCO₃ and ethylene urea. Gibbs free energy of formation (ΔG) and transition state energy (ΔG^{\ddagger}) in the parentheses are relative values with respect to that of the reactant (energies are in kca mol⁻¹). The two numbers in each parenthesis are energies calculated without and with solvent effect, respectively.

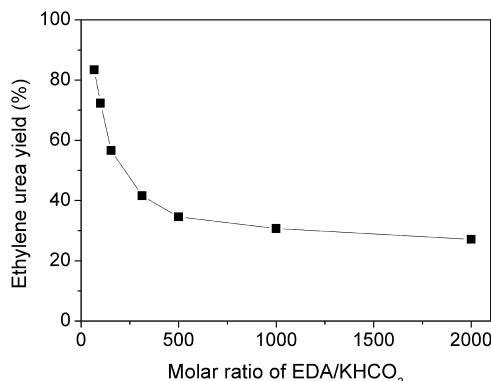


Fig. 7. Effect of the amount of KHCO₃ on the carboxylation of EDA by CO₂. Reaction condition: EDA (100 mmol), solvent (NMP, 20 mL), P_{CO₂} = 5 MPa, reaction temperature = 200 °C, amount of added ethylene urea = 1 g.

such as methanol and isopropanol (IPA), affording ethylene urea in yields of 5.2 and 2.3%, respectively. As discussed above, KHCO₃ functions as a proton donor as well as proton acceptor to and from the intermediate species formed from the reaction of EDA with CO₂. However, in the presence of an alcohol solvent, KHCO₃ seems to prefer interacting with the alcohol via hydrogen bonding interaction, thereby limiting the interaction of KHCO₃ with the intermediate species. In nonpolar solvents such as toluene and THF, negligible amounts of ethylene urea were produced, demonstrating the importance of the solvent polarity. It seems that the ionic transition and intermediate carbonation species formed from the reaction of EDA with CO₂ are destabilized in nonpolar solvents and thus easily dissociated back into EDA and CO₂ by losing CO₂ under experimental condition.

One may suspect that the carboxylation of EDA by KHCO₃ could proceed in a homogeneous way. To check the possible homogeneous reaction, a NMP (30 mL) solution containing KHCO₃ (10 mmol) with or without the added ethylene urea (2 g) was treated with 5.0 MPa of CO₂ at 200 °C and for 2 h in a 100 mL stainless steel bomb reactor equipped with a sampling port and a porous metal filter (see Fig. S1 in Supplementary data). After the period of 2 h, the reaction mixture was filtered at 200 °C under CO₂ pressure by opening the valve connected to the metal filter and the sampling port, and the filtrate was slowly transferred to a 90 mL high pressure glass bottle (Andrews Glass Co.), which was immersed in a water bath maintained at 20 °C. The resulting transparent solution collected in the glass bottle was loaded into another 100 mL stainless steel bomb reactor containing EDA (100 mmol), and the carboxylation reaction was carried out at 200 °C for 2 h under 5.0 MPa of CO₂ pressure. The GC analysis of the product mixtures showed that the yields of ethylene urea were 21.3% and 23.7% for the carboxylation conducted without and with ethylene urea, respectively. The yields of 21.3% and 23.7% are practically same as those achieved from the non-catalytic carboxylation reaction without and with the presence of ethylene urea (see Table 2), implying that the carboxylation of EDA by KHCO₃ proceeds in a heterogeneous way in NMP.

3.6. Influence of reaction temperature and CO₂ pressure

Table 4 shows the effects of temperature and CO₂ pressure on the KHCO₃-catalyzed carboxylation of EDA conducted in NMP for 2 h in the presence of added ethylene urea. The yield of ethylene urea increased with the increase of the temperature up to 200 °C, but decreased gradually thereafter. GC and GC-Mass analyses of the reaction mixture revealed that, at the temperature above 200 °C, unknown side products were formed in small quantities by the decomposition of ethylene urea and NMP. On the contrary, the

Table 4

Effects of the reaction temperature and pressure on the carboxylation of EDA by CO₂.^a

Temperature (°C)	P _{CO₂} (MPa)	Ethylene urea yield (%)
170	5	29.8
180	5	46.3
190	5	64.6
200	2	71.8
200	5	72.3
200	7	73.4
200	10	74.6
210	5	68.3
220	5	65.7

^a Reaction condition: EDA (100 mmol), molar ratio of EDA/KHCO₃ = 100, solvent (NMP, 20 mL), P_{CO₂} = 5 MPa, reaction temperature = 200 °C, reaction time = 2 h, amount of added ethylene urea = 1 g.

Table 5

Carboxylation reaction of diamines by CO₂.^a

Diamine	Cyclic urea yield (%) [*]	
	Without added ethylene urea	With added ethylene urea ^b
EDA	38.8 (87.5)	72.3 (95.3)
1,2-PDA	51.2 (96.7)	75.1 (98.4)
1,3-PDA	50.3 (95.5)	73.8 (98.2)

^{*} The numbers in parentheses are yields of cyclic ureas for 4 h reactions.

^a Reaction condition: diamine (100 mmol), molar ratio of diamine/KHCO₃ = 100, solvent (NMP, 20 mL), P_{CO₂} = 5 MPa, reaction temperature = 200 °C, reaction time = 2 h (4 h).

^b Amount of added ethylene urea = 1 g.

effect of CO₂ pressure was almost negligible. When the CO₂ pressure was varied from 2.0 to 10.0 MPa at 200 °C, the yield of ethylene urea was changed only by 2.8% from 71.8 to 74.6%.

3.7. Carboxylation of different diamines

The carboxylation reactions of 1,2-PDA and 1,3-PDA were also conducted in the presence of KHCO₃ with or without the added ethylene urea in NMP at 200 °C for 2 h. As listed in Table 5, in the absence of added ethylene urea, corresponding cyclic ureas were produced in yields around 50%. In contrast, the yields of cyclic ureas increased significantly to about 75% when ethylene urea was added in the beginning, again demonstrating the promoting effect of ethylene urea. Like in the carboxylation of EDA, the driving force for the carboxylation reactions of 1,2-PDA and 1,3-PDA seem to be the formation of stable 5- and 6-membered ring, respectively.

4. Conclusions

The carboxylation reactions of EDA, 1,2-PDA, and 1,3PDA were greatly accelerated when ethylene urea was present from the beginning of the reaction. The carboxylation of diamines with CO₂ in NMP in the presence of an alkali metal carbonate or bicarbonate catalyst such as KHCO₃, K₂CO₃, CsHCO₃ and Cs₂CO₃ exhibits a typical autocatalytic behavior. For instance, the rate of the carboxylation of EDA using KHCO₃ as a catalyst is found to increase sharply after a certain period of reaction time, showing a S-shaped curve. Experimental and theoretical calculation results reveal that such an autocatalytic behavior is originated from the synergy effect of KHCO₃ and ethylene urea produced during the carboxylation. By the presence of ethylene urea, the proton donating and accepting ability of the catalyst could be greatly enhanced. Ethylene urea seems to transform into enol form in the presence of a base catalyst like KHCO₃ under experimental condition, thereby enabling ethylene urea to function as a proton donor to the catalyst. The selection of solvent is particularly important in the base-catalyzed carboxylation of diamines with CO₂. The solvent employed should

be sufficiently polar enough to stabilize CO_2 -containing intermediate ionic species. Otherwise, the intermediate species will be easily dissociated back into diamine and CO_2 . Nonetheless, the use of protic solvents like alcohols should be avoided because they tend to interact strongly with the base catalyst via hydrogen bonding. As a result, the interaction of the catalyst with the CO_2 -containing species gets reduced, resulting in the decrease of the catalytic activity.

In summary, the rate of the carboxylation reactions of diamines to corresponding cyclic ureas can be facilitated when a catalyst is combined with a cyclic urea like ethylene urea in an appropriate polar aprotic solvent.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.02.079>.

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